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ScienceDirect

Energy Procedia 91 (2016) 1012 – 1017

Energy Procedia

SHC 2015, International Conference on Solar Heating and Cooling for Buildings and Industry

Polyvinyl alcohol-salt hydrate mixtures as passive thermal energy storage systems

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Abstract

Inorganic salt hydrates are promising candidates as latent heat storage materials entailing, for example, a high thermal energy storage density and cheap price [1,2] in spite that they have many handicaps. For almost all applications, Phase change materials (PCMs) have to be encapsulated, that is, they have to be hermetically sealed within barrier containments, preferably within small microcapsules. Encapsulation improves heat transfer, cycling stability, and material compatibility with the environment. However, no attempt has been completely successful to microencapsulate salt hydrates so far due to the high surface polarities of these substances, edge alignment effects, their tendency to alter their water content [3]. This work is aimed to encapsulate some commonly used salt hydrates; sodium sulphate decahydrate ($Na_2SO_4.10H_2O$) and calcium chloride hexahydrate ($CaCl_2.6H_2O$) in a hydrophilic polymer; polyvinyl alcohol (PVA) stably for passive thermal energy storage systems. So that an economically beneficial application mean will be validated.

Peer-review by the scientific conference committee of SHC 2015 under responsibility of PSE AG

Keywords: Thermal energy storage; Passive systems; Phase change materials; Salt hydrates

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Peer-review by the scientific conference committee of SHC 2015 under responsibility of PSE AG
doi:10.1016/j.egypro.2016.06.269

1. Introduction

Phase change materials (PCMs) used for thermal energy storage are generally non-toxic inorganic and organic products engineered for miscellaneous applications. Energy is stored as a combination of sensible and latent heat in Thermal Energy Storage (TES) materials. The latent heat storage occurs at isothermal conditions corresponding to the phase transition temperature of the PCM and is very attractive with considerably high energy storage density [4].

Inorganic PCMs are engineered hydrated salt solutions made from natural salts with water. Salt hydrates as PCMs have been among the most researched latent heat storage materials. Often salt hydrates are the lowest cost PCM only behind water and gel packs. Numerous trials and sub-scale tests have been carried out on these materials. The material comprises $M•nH_2O$, where M is an inorganic compound. The chemical composition of salts is varied in the mixture to achieve required phase-change temperature. Special nucleating agents are added to the mixture to minimize phase-change salt separation and to minimize super cooling, that are otherwise natural characteristic of hydrated salt PCMs. Salt hydrates are characteristic of being non-toxic, non-flammable and economical. Table 1 shows specific energy densities of some of PCMs. The energy density of salt hydrates comes from both the storage mechanism and the density of the materials [5,6].

Nomenclature

TES	Thermal energy storage
PCM	Phase change material
PVA	Polyvinyl alcohol
DSC	Differential scanning calorimeter
T-history	Thermal history
$CaCl_2.6H_2O$	Calcium chloride hexahydrate
$Na_2SO_4.10H_2O$	Sodium sulfate decahydrate

Table 1. Energy potential of some of widely investigated PCMs for thermal energy storage applications

Substance	Specific energy density [$kWh.m^{-3}$]
Water	34.5
Gravel	23.0
Paraffin wax	62.4
$CaCl_2 . 6H_2O$	117.4
$Na_2SO_4 . 10H_2O$	131.7

Salt hydrates brings about some drawbacks as well, while in usage. For example they incongruently melt leading to phase separation and supercooling because of their weak nucleation property. Anhydrous salts and aqueous solution of salts are formed as a result of dehydration process. They are considerably heavier than the solution and precipitate to the bottom of the container. During freezing, hydrates back at the solution-precipitate interface. Consequently, a contact barrier between the liquid and the anhydrous salt solution prevents reversible working. Accordingly, the bad crystallization of compound and the change in the thermophysical properties of the PCM arise. Phase separation can be prevented by adding some external agents to change the properties of the salt hydrate and thereby to hinder the anhydrous phase to sink. Gelling or thickening agents are the mostly studied solutions to overcome the above-mentioned drawbacks [7]. In this work, a hydrophilic polymer has been used to distribute the solid salt hydrate and some extra water in the matrix homogeneously in the heterogeneous system.

In spite of its several advantages and potential, inorganic PCMs are yet to be commercialized in a significant way. They were generally used in active systems. The performance of those in active systems depends on the processing condition. The reason behind not using them in passive system is their irreversible operating conditions. For passive systems, they have been packed in macroencapsulated metal containers and their long term usage brought about problems caused by their handicaps. To be used in passive system they should be evaluated in terms of individual microdomains preventing incongruent melting.

2. Experimental

Thermal energy storage systems should be composed of phase separated salt hydrate crystal domains in the matrix of the composite since the enthalpy bears as a result of the water release and uptake from the packed system but not in the solution. Therefore the composites have been prepared as heterogeneous slurries. The hydrophilic polymer is chosen to hold water consistent in the system after the release from the salt hydrate crystalline system. The ratio of hydrophilic polymer to salt hydrate is 1/10. Water is added to the system to confirm homogeneously distributed phase separated salt hydrate domains in polyvinyl alcohol. For homogeneous distribution, the composite materials are formed by mechanically mixing. Thermal properties of prepared PVA-salt hydrate mixtures have been investigated using a differential scanning calorimeter (DSC) instrument (Netzsch-DSC 214 Polyma). For the applicability, they have also been tested using Thermal history (T-history) system with 15 grams of samples. In addition, the thermal conductivities of materials were measured at 25 °C using a thermal property analyzer (Decagon devices, KD2 pro model).

3. Results and discussion

DSC curves of PVA-$Na_2SO_4.10H_2O$ and PVA-$CaCl_2.6H_2O$ with Cp-Temperature curves are represented in Fig. 1.The curves for the total enthalpy stored and released during the heating and cooling periods drawn using the DSC data (Fig. 1) are valuable to analyze the sensible and latent heat storage capacity of the materials together. Thermal properties, calculated using DSC investigations, of PVA-$Na_2SO_4.10H_2O$ and PVA-$CaCl_2.6H_2O$ were tabulated in Table 2. As seen in Table 2, PVA-$Na_2SO_4.10H_2O$ system stored and released much more energy than $CaCl_2.6H_2O$ system. It was attributed to the high solubility of $CaCl_2.6H_2O$ in the same amount of water. The same amount of water dissolved much more $CaCl_2.6H_2O$ than $Na_2SO_4.10H_2O$ and left lower amount of crystalline $CaCl_2.6H_2O$ for enthalpy development.

The difference of the enthalpy values in heating and cooling processes is attributed as instrumental because the values are reproducible in the second run. The phase change temperature of both of the systems suggests that these systems could be validated in green house protection systems. It may be noted that these systems start to change the phase at about 30 °C during heating which is important to protect plants from high temperatures and at around 5 °C during cooling which is important to protect the plants from freezing. One of the main problems of exploiting salt hydrates in passive systems is reproducibility of the data which is overcame here by putting the salt hydrates with some extra water in a hydrophilic polymer. The extra water acted as a continuous water supply for microphase separated salt hydrates distributed along the system in regaining the hydration water from the surroundings. In small size domains of the phase separated salt hydrates helps particles to penetrate water inside the particles in the usage time period.

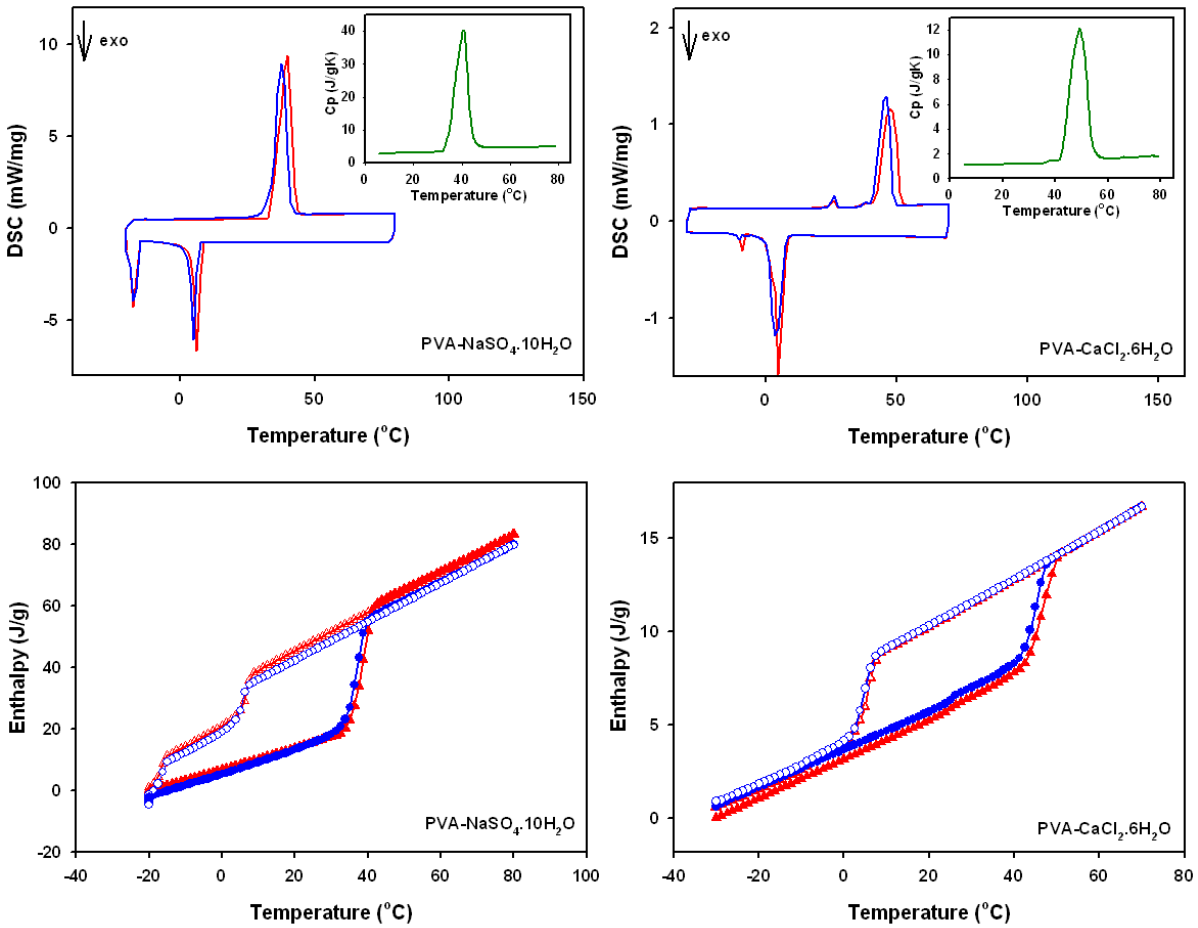

Fig. 1. The DSC curves of the PVA-Na_2SO_4.10H_2O (upper left) with C_p-Temperature curve (in the box) and PVA-$CaCl_2$.6H_2O (upper right) with C_p-Temperature curve (in the box) and total enthalpy curves drawn from the DSC data for PVA-Na_2SO_4.10H_2O in the lower left and for PVA-$CaCl_2$.6H_2O in the lower right.

Table 2. DSC data of PVA-Na_2SO_4.10H_2O and PVA-$CaCl_2$.6H_2O polymer-salt hydrate composite systems

Sample	Period	T (Start)	T (Peak)	Entalpy
PVA-Na_2SO_4.10H_2O	Heating	34.2	37.7	248.7
	Cooling	1.4	-1.2	-207.6
PVA-$CaCl_2$.6H_2O	Heating	42.1	47.3	80.0
	Cooling	7.3	4.2	-60.0

For evaluation, the quality of a PCM, not only the overall latent heat but also the shape of the melting and cooling curves is important [8]. This is discussed by total enthalpy plots. It can be seen that both of the systems absorbed the latent heats in one steps as PVA-Na_2SO_4.10H_2O released in 2 steps (one at very low temperature) and PVA-$CaCl_2$.6H_2O released in one step. However the energy stored in PVA-Na_2SO_4.10H_2O system is much higher than PVA-$CaCl_2$.6H_2O system. Each plot is shown for two experiments in order to prove the reproducibility in the experiments.

Temperature history analysis of the thermal energy systems reveals application characteristics. The T-history graphs were drawn for both materials system during heating (Fig. 2 left curves) and cooling (Fig. 2 right curves) in a

constant temperature environment. The environment medium temperatures were maintained constant at 45 °C and -10 °C during heating and cooling, respectively. The heating graphs show that in both PVA-Na_2SO_4.10H_2O and PVA-$CaCl_2$.6H_2O systems heat protected at around phase change temperatures of the salt hydrates as they release the latent heat during cooling. Cooling occurred fast as shown in T-history measurements during the cooling (Fig.2 right curves). Therefore the plateau of cooling curves was not detected easily as in heating curves.

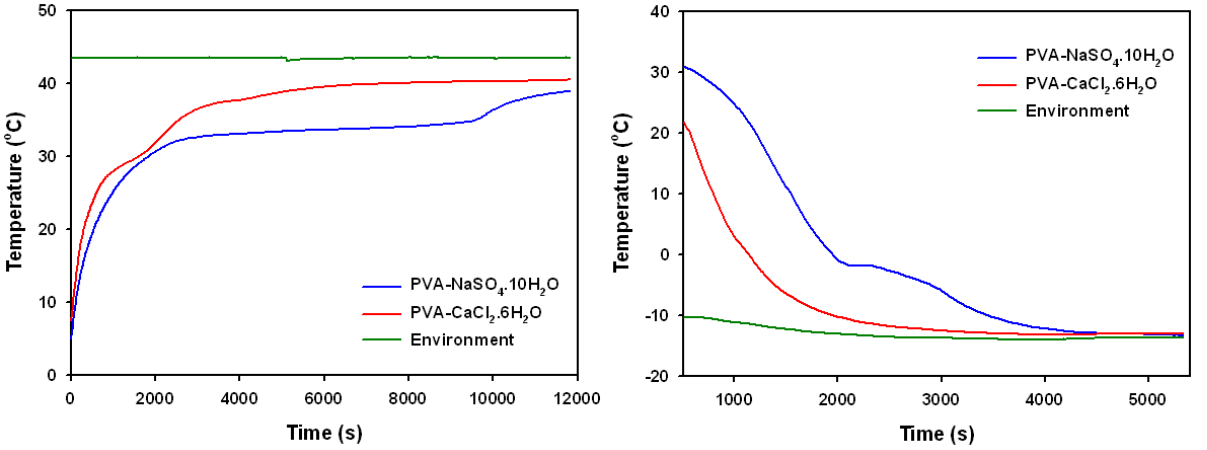

Fig. 2. The T-history curves of the PVA-Na_2SO_4.10H_2O and PVA-$CaCl_2$.6H_2O polymer-salt hydrate systems (left curves for heating period, right curves for cooling period). Green lines: medium (environment) temperature, Blue lines: PVA-Na_2SO_4.10H_2O, Red lines: PVA-$CaCl_2$.6H_2O

The time of temperature increase retardations are approximately 40 and 15 minutes for PVA-Na_2SO_4.10H_2O and PVA-$CaCl_2$.6H_2O systems respectively refer the appropriate Fig. It is because of thermal storage capacity and thermal conductivity of PVA-Na_2SO_4.10H_2O and PVA-$CaCl_2$.6H_2O systems. The reason for shorter response time of PVA-$CaCl_2$.6H_2O system is not only because of lower enthalpy than PVA-Na_2SO_4.10H_2O system but also because of higher thermal conductivity with the same amount of water as represented in the following figure. Thermal conductivity is another important aspect that determines the response efficiency of thermal storage materials. Low thermal conductivity of a PCM means low heat transfer rate during the storage and release processes of LHTES systems.

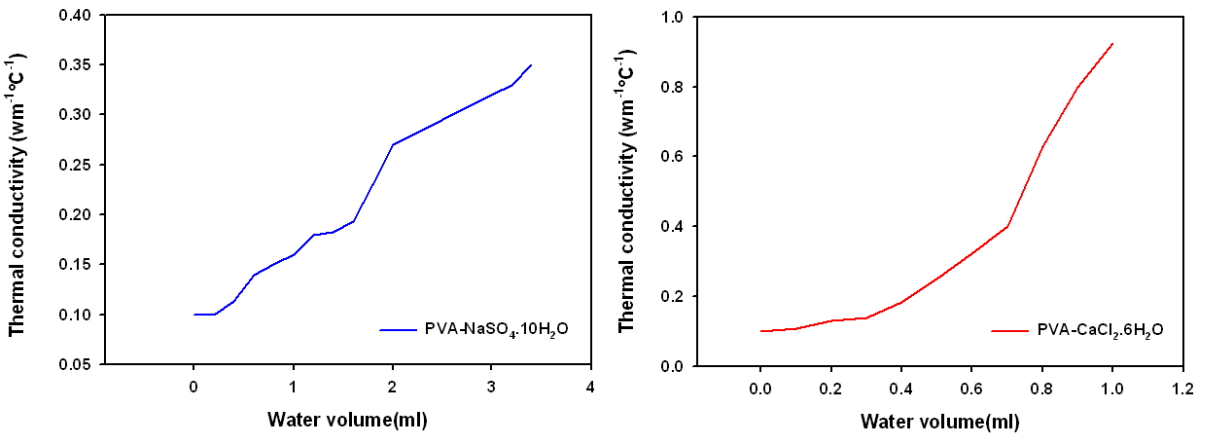

Fig. 3. Thermal conductivity variation of PVA-Na2SO4.10H2O and PVA-CaCl2.6H2O systems with the water content

Water in the phase change systems increased thermal conductivity as it decreases the crystal amount of salt hydrate by solving some parts clarity. The source of energy storage is the water stacked in the crystals and when the

crystals dissolve the latent heat stored and released during the phase change process decreases. Due to that the solubility of $CaCl_2.6H_2O$ in water is much higher than the solubility of $Na_2SO_4.10H_2O$, the enthalpy of PVA-$CaCl_2.6H_2O$ is more affected by the water amount. On the other hand the salt concentration of the solution increases the thermal conductivity. It increases in PVA-$CaCl_2.6H_2O$ system much more than PVA-$Na_2SO_4.10H_2O$ system with increasing water amount in the composites due to the solubility difference.

It can be seen from Fig. 3 that reasonable values comparable to some organic PCMs such as paraffins, fatty acids, and esters with thermal conductivities in the range of 0.16–0.19 W/m K at solid state were measured. Besides the thermal conductivity of the PVA-$Na_2SO4.10H_2O$ and PVA-$CaCl_2.6H_2O$ systems could be easily and cheaply changed with water amount. Furthermore and additive increasing the thermal conductivity of water could increase thermal conductivity of such systems.

4. Conclusions

- Various process system designs are reviewed in order to develop a framework and a microphase separated salt hydrate system in hydrophilic polymer with some water consistent in the system has been used. These blends were successfully produced by mechanical mixing of salt hydrate added hydrophilic solution. This is a thermo-chemical model for association and dissociation of salt hydrate is developed. This has to be linked with an under-development model for heat storage.

- Hydrophilic polymers-salt hydrate slurries prepared solved some of the salt hydrate usage problems like irreversible exploitation and corrosion.

- From the results presented, it was concluded that PVA-Na2SO4.10H2O and PVA-CaCl2.6H2O systems could be considered as promising passive thermal energy storage systems for green house and food freeze- overheat protection.

Acknowledgements

The author would like to acknowledge the support to INOTES project in the scope of EU ERA NET New Indigo Program funded by Scientific and Technological Research Council of Turkey (TÜBİTAK, Project No.: 114M121), by the German Bundesministerium für Bildung und Forschung (the German Federal Ministry of Education and Research) for financial support under project (No. 01DQ14009) as well as by the Indian Funding Agency.

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